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AUTHOR(S):

Sasaki, Yoshihiro

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Extractive Spectrophotometric Determination of Iron(II) with 2,6-[1-(2-Methoxyethylimino)ethyl]pyridine and Sodium Picrate

Yoshihiro SASAKI*

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A method for ion-pair extraction and determination of iron with 2,6-[1-(2-methoxyethylimino)ethyl]pyridine, meep, and sodium picrate, Napic, is described. Iron is extracted into nitrobenzene in the form of $\text{Fe}(\text{meep})_2(\text{pic})_2$ ($\lambda_{\text{max}}=596 \text{ nm}$, $\epsilon=1.22 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Absorbance follows Beer's law up to $68 \mu\text{g}$ iron in 10 cm^3 nitrobenzene. The interference of diverse ions is removed by masking, but Co^{2+} ion interferes severely. The method is applied to determine iron in an aluminium compound and natural water.

KEY WORDS: Spectrophotometric Determination/ Iron(II)/ Aluminium Compound and Natural Water/

It is well-known that hydrazones, Schiff bases and oximes are useful in detection and determination of metal ions.¹⁾ Recently, analytical applications of hydrazones have been extensively tested.^{2,3)} Such types of hydrazones, Schiff base and oximes derived from 2,6-diacetylpyridine, dacpy, as shown in Fig. 1 are also thought to have potential ability for colorimetric or fluorimetric reagents.⁴⁾ The reagents are characterized by the functional groups increased in number. 2,6-Diacetylpyridinedioxime

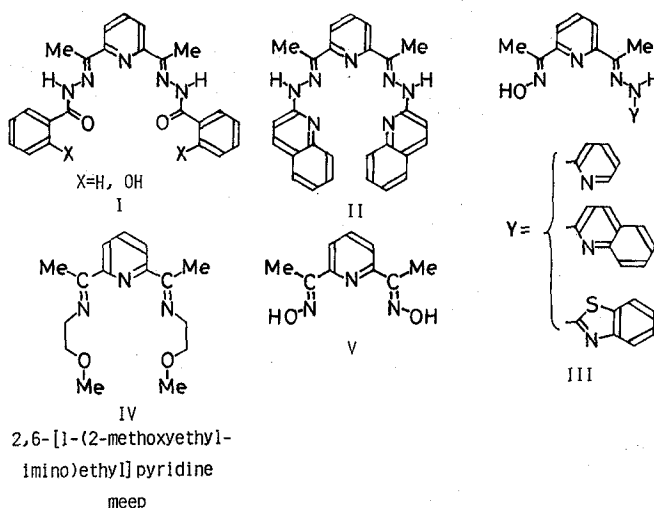


Fig. 1. Hydrazones, Schiff base and oximes derived from 2,6-diacetylpyridine.

* 佐々木義弘: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

has been applied to the determination of iron in alkaline medium.⁵⁾ Nelson *et al.* have characterized iron(II), cobalt(II) and nickel(II) complexes with Schiff bases synthesized from dacypy and alkylamines.⁶⁾ The Schiff bases function as tridentate ligand. In this paper, the color reactions of 2,6-[1-(2-methoxyethylimino)ethyl]pyridine, meep, with some metal ions are described and a photometric method for determining trace amounts of iron is proposed.

EXPERIMENTAL

The Schiff base, meep, was synthesized from 2,6-diacetylpyridine (Aldrich) and 2-methoxyethylamine according to Nelson *et al.*⁶⁾ (Found: C, 64.82; H, 8.22; N, 15.07%). Several metal complexes with meep were prepared as picrate by a similar procedure to that reported by Nelson *et al.*⁶⁾ (Found: C, 46.52; H, 4.83; N, 15.83% for Fe(II)(meep)₂(pic)₂, C, 46.77; H, 4.54; N, 15.56% for Co(II)(meep)₂(pic)₂, C, 46.75; H, 4.55; N, 15.55% for Cu(II)(meep)₂(pic)₂, and C, 46.51; H, 4.56; N, 15.63% for Ni(II)(meep)₂(pic)₂ (pic: picrate anion)).

The meep solution was prepared by dissolving the reagent in nitrobenzene (3×10^{-2} M (1 M = 1 mol/dm³)). A 2.03×10^{-2} M iron(II) solution was prepared by dissolving 820 mg of ammonium iron(II) sulfate hexahydrate in 100 cm³ of 0.06 M hydrochloric acid. 2.5×10^{-2} M Sodium picrate and fresh 1% ascorbic acid solutions were prepared.

Absorbance and absorption spectra were measured with a Shimadzu Model UV 180 spectrophotometer (1 cm quartz cells). The pH measurements were made on a Toa Electronic HA-15A digital pH meter. Shaking of solutions for solvent extraction was made on a Iwaki KM type shaker.

Standard Procedure. Transfer 150 cm³ of sample solution, whose pH is adjusted to 1 by hydrochloric acid, into a separating funnel. Add 1.5 cm³ of 1% ascorbic acid and 3 cm³ of 2.5×10^{-2} M sodium picrate, and stand the solution for 5 min. Adjust pH of the solution to the range of 3.2–3.9 by sodium hydroxide. Add 10 cm³ of 3×10^{-2} M meep to the solution, shake the funnel for 3 min and filtrate the organic layer with a filter paper (No. 5A). Measure the absorbance against the reagent blank at 596 nm.

RESULTS AND DISCUSSION

The Schiff base, meep, was very soluble in organic solvents such as nitrobenzene and chloroform. The reagent was stable in the solvents, but it was hydrolyzed in water. It formed water-soluble complexes with Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺ ions, and the complexes were isolated in the form of M(II)(meep)₂(pic)₂ (M = Fe, Co, Ni and Cu). The absorption spectra of the complexes in benzonitrile are shown in Fig. 2. The copper and nickel complexes did not exhibit prominent absorption bands in the wavelength range of 500–650 nm. The cobalt and iron complexes exhibited absorption bands at 550 nm (log ϵ = 3.3) and at 596 nm (log ϵ = 4.1), respectively. The metal ions in aqueous solutions were extracted into nitrobenzene in the presence of sodium picrate, Napic, and meep. The spectra of the extracted complexes of

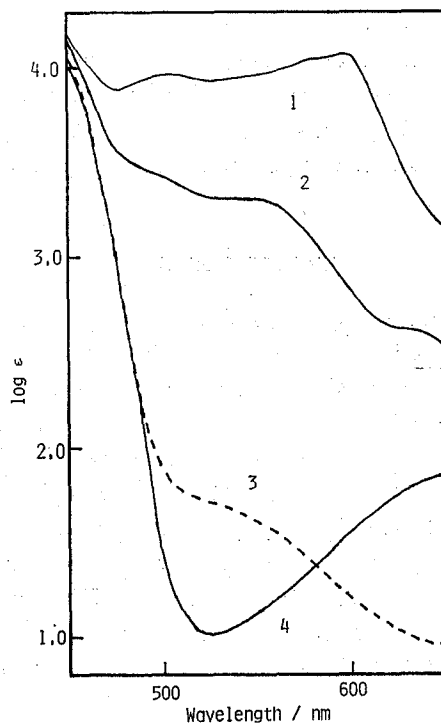


Fig. 2. Absorption spectra of meep complexes in benzonitrile.

1: $\text{Fe(II)(meep)}_2(\text{pic})_2$, 2: $\text{Co(II)(meep)}_2(\text{pic})_2$,
3: $\text{Ni(II)(meep)}_2(\text{pic})_2$, 4: $\text{Cu(II)(meep)}_2(\text{pic})_2$.

iron(II) and cobalt(II) were consistent with those in Fig. 2.

Fundamental Studies for Determination of Iron. The absorbance at 596 nm was used for determination of iron. The complex was stable for at least 95 h. A maximum constant absorbance was obtained in the pH range of 3.0–4.0 (Fig. 3).

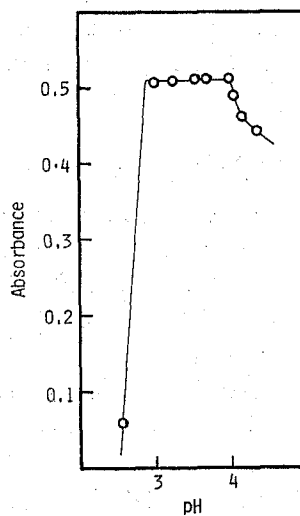


Fig. 3. Effect of pH on absorbance of the extracted complex for 23 μg of iron.

Ascorbic acid was used as a reducing agent. Iron(III) was perfectly reduced to iron(II) within 5 min by adding 1–2 cm³ of 1% ascorbic acid to the sample solution. When more than 3 cm³ of the reducing agent solution was added, the absorbance was decreased. Hydroxylamine hydrochloride was not used because the reagent reacts with meep to give 2,6-diacetylpyridinedioxime.

The influences of the concentrations of meep in nitrobenzene phase and Napiç in aqueous phase were studied independently. A constant absorbance was obtained in the meep concentration of more than 5×10^{-3} M and in the Napiç concentration of more than 3.3×10^{-5} M for 23 μ g of iron, respectively. The shaking time was varied from 1 to 10 min. This variation did not produce any change in absorbance. The effect of the volume of aqueous phase was studied in the volume range of 10–500 cm³, and any effect on absorbance was not found.

A calibration curve was prepared under the condition described above. The curve obeys Beer's law up to 68 μ g of iron in 10 cm³ of nitrobenzene. The molar absorption coefficient and Sandell's sensitivity were 1.22×10^4 dm³ mol⁻¹ cm⁻¹ and 4.6×10^{-3} μ g cm⁻², respectively. The relative error of the method was 0.8%.

The spectrum of the extracted complex was consistent with that of the prepared complex, Fe(II)(meep)₂(pic)₂, in benzonitrile. The result of the continuous variation method studied under the condition of a constant meep concentration showed a stoichiometric ratio of iron to pic of 1:2 (Fig. 4). These suggest that iron(II) is extracted in the form of Fe(meep)₂(pic)₂ into nitrobenzene.

For the determination of 23 μ g of iron by this method, the diverse ions can be tolerated at the levels given in Table I. The limiting value was taken as that value which caused an error of not more than 5% in absorbance. The interference of many metal ions was removed by masking. Co²⁺, being extracted at the same time, interfered severely.

The present method was applied to the determination of iron in aluminium nitrate (Sample 1) and river water (Sample 2). Sample 1 was prepared by dissolving a weighed amount of Al(NO₃)₃·9H₂O (guaranteed reagent grade) into 0.1 M

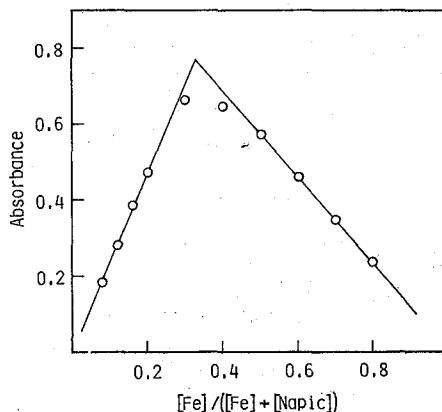


Fig. 4. Continuous variation method.
 $[\text{Fe}] + [\text{Napiç}] = 1.47 \times 10^{-5}$ M,
 $[\text{meep}] = 10^{-2}$ M, pH=3.9.

Ion-Pair Extraction and Spectrophotometric Determination of Iron(II)

Table I. Tolerance limits of diverse ions

Diverse Ion	Tolerance limit
K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Br^- , Cl^- , F^- , I^- , SO_4^{2-} , NO_3^- , $S_2O_3^{2-}$, SCN^- , Acetate, Tartrate	2.3 g
Citrate, Dimethylglyoxime	23 mg
CN^-	230 μg
EDTA	2.3 μg
Ag^{+1} , Al^{3+2} , Pb^{2+1} , Cd^{2+3} , Cr^{3+4}	23 mg
Ni^{2+}	12 mg
Mn^{2+} , Zn^{2+} , Sn^{2+2}	2.3 mg
Cu^{2+4}	230 μg
Co^{2+}	23 μg

Iron taken: 23 μg .

Masking Agent: 1) 10 cm³ of 2×10^{-1} M sodium thiosulfate, 2) 10 cm³ of saturated sodium fluoride aqueous solution, 3) 10 cm³ of 1.8 M sodium iodide, 4) 10 cm of 2 M sodium thiocyanate

Table II. Determination of iron in aluminium nitrate and river water

Sample	Iron found	
$Al(NO_3)_3 \cdot 9H_2O$	13.8 ± 0.1 ppm ¹⁾	13.9 ± 0.3 ppm ²⁾
River water (Kizu River, Kyoto Pref.)	0.518 ± 0.003 mg dm ^{-3 1)}	0.498 ± 0.001 mg dm ^{-3 3)}

1) meep method, 2) 1,10-phenanthroline method, and 3) 4,7-diphenyl-1,10-phenanthroline method.

hydrochloric acid. In order to prevent interference due to Al^{3+} ion, 10 cm³ of saturated sodium fluoride aqueous solution was added. Sample 2 was taken from Kizu River and its pH was adjusted to 1 by hydrochloric acid immediately. The sample was filtered through millipore filter (1.2 μm); the filtrate was analyzed for the total iron content. The analytical data are tabulated in Table II. The values agreed well with the results obtained by 1,10-phenanthroline⁷⁾ and 4,7-diphenyl-1,10-phenanthroline⁸⁾ methods. The present method has a high selectivity, but the sensitivity of the method is comparable to that of 1,10-phenanthroline method.⁹⁾ The proposed method may be successfully applied to the determination of iron in environmental samples because iron can be easily concentrated by means of the solvent extraction.

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